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Aerobic Epoxidation of Hindered Olefins and Enol Ethers Catalyzed by a Polymerizable β-Ketoesterate Complex of Iron(III).

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Abstract: Peculiar hindered olefins and derivatives have been epoxidized, under Mukaiyama's conditions, using iron(III) catalytic centres. The experimental results allow to rule out the involvement of singlet oxygen and free peroxyacids as active species.

A new intriguing procedure for the epoxidation of a great variety of olefins and derivatives, based on β-diketonato complexes of nickel(II) or iron(III) in the presence of aldehydes and molecular oxygen, has been recently proposed by Mukaiyama and coworkers[1] (scheme 1).

Scheme 1
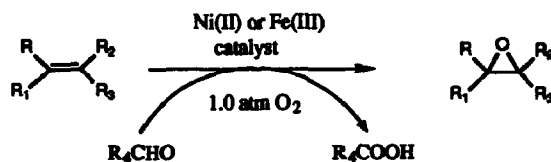
With the exception of the report that the active species, involved in the above epoxidation procedure, should not be a simple peroxyacid, generable from aldehydes by autoxidation[1a], no further comment concerning the actual mechanism was reported.

In this regard, more recently, Nishida *et al.*[2] claimed that singlet oxygen-like active species could be the key compounds for the epoxidation of olefins. This statement was based on the experimental observation that the reaction mixture of nickel(II) β-diketonato complex, aldehyde and oxygen exhibited high reactivity towards tetraphenylcyclopentadien-1-one, regarded as a singlet oxygen quencher, but not as a potential oxidizable substrate.[3] On the other hand, Kaneda *et al.* reported that the system consisting simply of molecular oxygen and aldehyde (isobutyraldehyde) oxidized, at 40 °C, several olefins to give the corresponding epoxides in high yields.[4]

Because of the important nature of such claims, with respect to the problem of oxygenation reactions, we decided to investigate Mukaiyama's oxidation reaction, extending our research on the aerobic epoxidation of olefins by polymerizable β-ketoesterate iron(III) complexes to peculiar unsaturated substrates such as methoxy-(2-naphtyl)-methylideneadamantane 1a,[5,6] iso-propylideneadamantane 1b,[7] benzhydrylideneadamantane 1c, fluorenylideneadamantane 1d and tetraphenylethylene 1e, frequently studied in $^1O_2$ oxygenations,[7,8] as well as in peroxyacid oxidations.[9]

The general epoxidation procedure is attractively simple: the olefinic substrates 1a-e (2.5 mmoles), the sacrificial iso-butyraldehyde (7.5 mmoles) and catalytic amounts (0.020 mmoles) of Fe(AAEMA)$_3$[10] [AAEMA= deprotonated form of 2-(acetoacetoxy)-ethylmethacrylate)] were stirred in 1,2-dichloroethane (10 ml), under oxygen atmosphere, at room temperature and daylight. The reactions, followed by gc/ms spectrometry, showed the formation of new products, whose fragmentation patterns were consistent with those of pure epoxides 2a-e, independently prepared.[9,11] After suitable reaction times (6-18 h) and quantitative conversions for all the substrates but for 1e (conv = 50%), the reaction products were isolated by column chromatography (silica gel, hexane/diethylether 5/1 as eluents), and fully characterized by ms, ir, ^1H and ^{13}C nmr spectroscopy.[11] Relevant results are collected in Table 1 whereas the structures of the starting materials and reaction products are depicted in Scheme 2.

Table 1. Epoxidation of Olefinic Compounds (2.5 mmoles) in the presence of i-butyraldehyde (7.5 mmoles) and Fe(AAEMA)3 (0.020 mmoles) in 1,2-dichloroethane (10 ml) under molecular oxygen (1 atm) at room temperature.

Entry	Substrate	Time (h)	Conversion (%)	Products (Yield %)
1	1a	18	100	2a (quant.)
2	1b	8	100	2b (quant.)
3	1c	6	100	2c (quant.)
4	1d	15	100	2d (15) + 3d (85)
5[a]	1d	15	100	2d (60) + 3d (40)
6	1e	18	50	2e (50) + 3e (45)
7[a]	1e	18	10	2e (70) + 3e (27)

[a]: in the absence of Fe(III) catalyst.

In two cases, i.e. with substrates 1d-e, together with the expected epoxides 2d (15 %) or 2e (50 %), large amounts of spiro [2H-adamantyl-2,9'(10'H)-phenantren]-10'-one 3d (85%)[12] and triphenylmethyl-phenylketone 3e (45 %) were also formed.

Although the carbonyl compounds 3d-e might derive by a protic acid isomerization of the corresponding pure epoxides 2d-e, however, our experimental results substantiate that such an isomerization does not occur. In fact, by prolonging the reaction time after the maximum conversion of the olefins was reached, no change in the (epoxide/ketone) ratio was observed .

Scheme 2
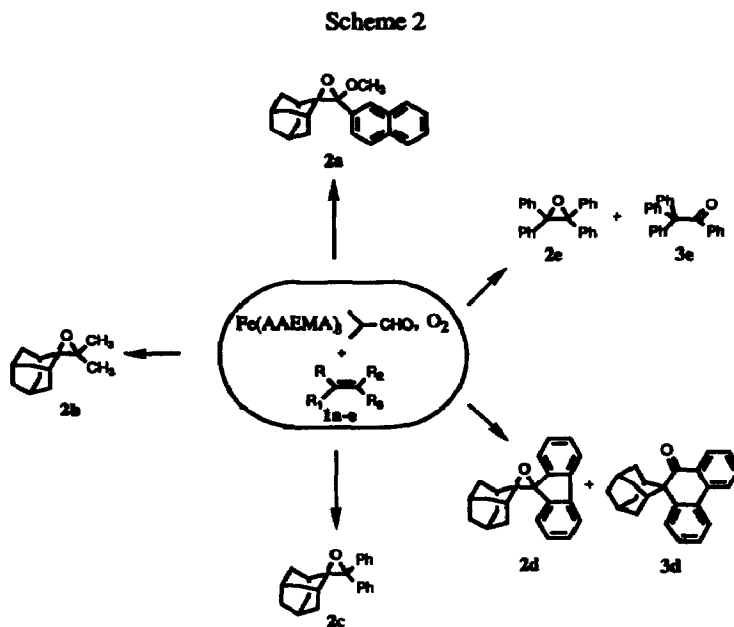
The oxiranes 2a-e did not suffer from further oxidation, since no appreciable amounts of products (2-adamantanone and methyl naphtoate, 2-adamantanone and acetone, or fluorenone and benzophenone), formally deriving from cleavage of C=C bond, were observed by gc/ms spectrometry.[13]

The same efficiency and selectivity was observed in similar reactions carried out in the dark.

The previous experimental results rule out the involvement of singlet oxygen, as the key reactive species. In fact, photosensitized and chemical oxygenation procedures involving $^1O_2$ easily convert the substrates 1a-c into the corresponding 1,2-dioxetanes.[7,8]

A remarkably different selectivity, was observed in the reactions performed on substrates 1d-e in the absence of the metal catalyst. In fact, these latter were converted, respectively, into mixtures of 2d (60 %) together with 3d (40 %) or 2e (70 %) together with 3e (27 %), see entries 5,7 of table 1.

The very high stability of the spirooxiranes 2a-d during the reaction time, even in the presence of renewed catalytic system, would also rule out an important involvement of *free* peroxyacids in the reaction medium. In fact, when an *m*-chloroperbenzoic acid (*m*-CPBA) epoxidation procedure is applied, expecially to substrate 1a, the initially formed oxirane 2a undergoes a fast acid-catalyzed rearrangement to give α-alkoxy or α-hydroxy ketone,[9a] never observed in our system.

By performing metal-catalyzed reactions on 1e in the presence of hydroquinone, employed as radical scavenger,[14] we observe the same mixture of products 2e (58 %) and 3e (40 %), but a significantly lower conversion (13 %) with respect to that (50 %) observed in the unmodified catalytic system, after the same reaction time.

In conclusion, although further detailed investigations in the area are warrented, these preliminary results seem point out the following facts: (a) the autoxidation of sacrificial aldehyde leads to a *free* peroxyacid species, which acts as the epoxidizing agent, even at room temperature; (b) the β-ketoesterate complex might catalyze the generation of a different percarboxylic species, plausibly a percarboxylic radical, perhaps

coordinated to the metal centre. In this regard, the occurrence of a more important isomerization in the epoxidation of internal olefins, such as *cis-* and *trans-* 2-octene, carried out by us in the presence of the iron(III) catalyst, can be taken as a clue of a non-concerted radical process.

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5.   The substrates **1a, c, d** have been synthesized by following Mc Murry's procedure, see ref. 6. The substrate **1b** has been synthesized accordingly to Adam's procedure, see ref. 7.

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11. The isolated reaction product **2a** shows physical and spectral data consistent with those reported for the same product in the ref. 9a.

     2b: m.p; 36°C; ir (KBr): υ = 3007, 2948, 1451, 1378, 1356, 957, 900, 729, 691 cm⁻¹;

     ¹H nmr (CDCl₃): δ =2.05-1.12 (m, 20 H) ppm; ¹³C nmr (CDCl₃): δ = 70.91, 63.27, 36. 69, 36.61, 36.50, 34.72, 32.47, 29.90, 26.82, 20.09, 20.03 ppm; ms (m/e %) 150 (100), 135 (15), 134 (14), 105 (24) 92 (52), 91 (51), 79 (39), 78 (15), 77(26), 67 (12), 65 (10), 55 (10), 43 (20), 42 (10), 41 (43).

     2c : white crystals from benzene/ethanol, m.p. 186-187°C; ir (KBr): υ = 3021, 2859, 1496, 1450, 940, 900, 747, 705 cm⁻¹; ¹H nmr (CDCl₃): δ = 7.57-7.55 (m, 4H), 7.53-7.17 (m, 6H), 2.05-1.53 (m, 14H) ppm; ¹³C nmr (CDCl₃): δ = 140.04, 128.38, 127.99, 126.96, 126.76, 126.64, 36.64, 35.89, 35.33, 32.38, 27.01, 26.71 ppm; ms (m/e %) 316 (65), 315 (56), 211 (12), 166 (90), 165 (100) 105 (17), 77 (20).

     2d: m.p. 135-136°C from benzene/ethanol; ir (KBr): υ = 3061, 2989, 2915, 1446, 965, 892 cm⁻¹;

     ¹H nmr (CDCl₃): δ = 7.74-7.70 (m, 2H), 7.41-7.34 (m, 4H), 7.25-7.17 (m, 2H), 3.52-1.20 (m, 14 H) ppm; ¹³C nmr (CDCl₃): δ = 141.89, 140.85, 128.41, 126.20, 124.07, 120.11, 73.55, 73.81, 36.38, 36.04, 35.40, 32.04, 26.77, 26.33 ppm; ms (m/e %) 314 (100), 298 (11), 215 (7), 194 (17), 181 (16), 180 (31), 165 (17), 121 (20), 91 (14), 79 (12), 77 (8).
     2e has been characterized by comparison with a pure sample.

12. **3d**: white crystals from benzene/ethanol, m.p. 164°C; ir (KBr): υ = 3062, 3025, 1691, 1598, 1473, 1291, 1242, 937, 765, cm⁻¹; ¹H nmr (CDCl₃): δ = 7.69-7.15 (m, 8H), 2.82-1.42 (m, 14H) ppm;

     ¹³C nmr (CDCl₃): δ = 210.21, 141.83, 137.84, 134.11, 132.60, 132.07, 128.83, 128.28, 127.12, 126.82, 126.28, 125.76, 121.21, 57.32, 39.99, 37.76, 35.07, 34.92, 34.54, 33.43, 29.43, 27.61, 27.37 ppm; ms (m/e %) 314 (100), 231 (18), 194 (41), 178 (17) 165 (26), 121 (8), 79 (16).
     The substrate **3e** has been characterized by comparison with a pure sample.

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